Signature of Martensite transformation on conductivity noise in thin films of NiTi shape memory alloys

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Slow time-dependent fluctuations, or noise, in the electrical resistance of dc magnetron sputtered thin films of Nickel Titanium shape memory alloys have been measured. Even in equilibrium, the noise was several orders of magnitude larger than that of simple diffusive metallic films, and was found to be non-monotonic around the martensitic transformation regime. The results are discussed in terms of dynamics of structural defects, which also lay foundation to a new noise-based characterization scheme of martensite transformation.

Growing interest in thin films of Nickel-Titanium (NiTi) shape memory alloys have been driven by many applications such as micropumps, microactuators for micro-valves and micro-positioners, etc.[1,2]. The thermoelastic martensite transformation causes shape memory effect as well as pseudo-elasticity, which makes these systems excellent actuation elements in microelectromechanical designs. However, in the thin film form, the diffusionless structural transformation from the high temperature (cubic B2: CsCl) austenite phase to low temperature (monoclinic B19/B19$'$) martensite phase[3] may be influenced by external parameters including the substrate, finite grain size, surface defects etc.[4], which often pose difficulty in probing the intrinsic structural dynamics in an unambiguous manner. The information from differential scanning calorimetry (DSC), Xray diffraction (XRD), scanning thermal microscopy (SThM), acoustic emission measurements etc.[2,5], are often limited, and it is desirable to have a more microscopically intuitive understanding of the martensite dynamics and corresponding temperature scales.

Here, we employed a new technique to characterize the martensite phase in thin NiTi films. The technique is based on measuring the time-dependent low-frequency fluctuations, or noise, in electrical resistivity (ρ) at fixed temperatures (T) at various stages of the austenite-to-martensite phase transition. Since electronic transport properties are directly affected at the martensite transition, for example, by the change in structural and scattering properties, or that in the density of states at the Ti sites due to the lowering in energy of the B19/B19$'$ structure, the time-averaged ρ vs. T has long been used as an empirical indicator of martensite transition[6]. Equilibrium resistance noise arises from the coupling of electron transport to slow variations in the configuration of structural disorder including migration/rotation of defect or atomic species, scattering off slow fluctuators or

two-level systems etc. While noise at stress-induced re-orientation in the martensite phase of free-standing NiTi wires has been measured before[7], no systematic investigations exist on the signature of martensite formation on equilibrium T-dependence of noise. Such a study would probe the influence of grains and grain boundaries on the thermoelastic properties of the NiTi films, and provide independent and microscopically intuitive estimates of the temperature scales of martensite transformation that may be relevant to growing applications of NiTi thin films.

The samples were prepared by dc magnetron sputtering of a mosaic target which consists of patterned Titanium disk of 76 mm diameter and 0.8 mm thickness laminated over a circular Nickel disk of 76 mm diameter and 1.6 mm thickness. Si (100) cleaned with dilute HCl and methanol were used as substrates. Two samples (S1 and S2) were deposited under similar conditions (Ar pressure of 2×10^{-3}mbar) with thicknesses 0.9μm and 1μm respectively, but annealed at dissimilar temperatures (480° C and 400° C respectively) that resulted in different levels of surface defects. The samples were characterized using XRD and scanning tunnelling microscopy (STM), which indicated coexistence of martensite and austenite phases at room temperature, with grain size $\sim$ 160nm. STM studies also indicated higher rms surface roughness in S2 than in S1. To measure noise, we have used a 5-probe ac measurement technique[8,9] with a resolution in the noise power spectral density (S_V) of $\approx 1 \times 10^{-20}$ V^2/Hz. The background noise primarily consists of the Johnson's noise, and atleast two orders of magnitude lower than the device noise at all T.

Although both samples show qualitatively similar metallic behavior and characteristic hysteresis, resistivity (ρ) data in Fig. 1 indicates ρ in S2 to be more than one order of magnitude higher than that of S1 confirming the presence of excess disorder scattering. In both cases the rise in ρ around 320 K on the cooling cycle implies formation of the R-phase on going from the cubic B2 (austenite) to the monoclinic B19$'$ (martensite) crystal structure[1]. We note that (1) in spite of large difference in ρ, the absolute magnitude of the hysteresis
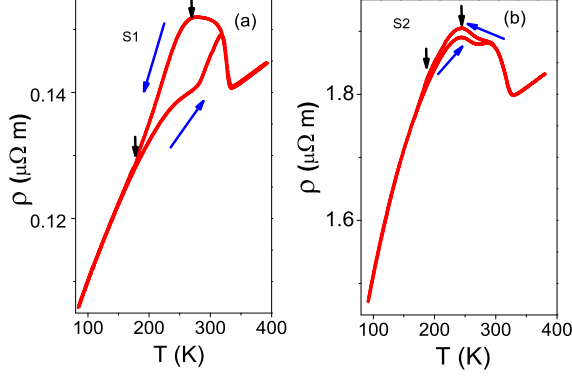
FIG. 1: Resistivity vs Temperature curves for (a) S1 and (b) S2. The arrows indicate the heating and cooling directions. M_s and M_f are also indicated by arrows.

FIG. 2: (a)Resistivity Fluctuations for heating, at temperatures 110 K, 260 K and 360 K as a function of time. (b) Normalised Power Spectral Density as a function of frequency, for the three temperatures. Note that the behavior is $1/f^\alpha$, $\alpha \sim 1$-1.2 at all temperatures. α (at $1 Hz$) vs T is plotted in the inset.

in ρ is similar for both samples. This confirms that the excess disorder in S2 only enhances the disorder density and the scattering rate, without substantially affecting the structural morphology of the system. (2) Secondly, the martensite start and finish temperatures can also be identified in the conventional manner[2], which turn out to be $M_s \approx 270K$ and $M_f \approx 180K$ for S1 and $M_s \approx 245K$ and $M_f \approx 190K$ for S2.

In order to focus on the equilibrium dynamics in the films, the noise was measured at fixed T (stabilized to an accuracy of 3 ppm) after a waiting period of 1800 - 2000 sec at each T. Fig. 2 shows typical time-dependent fluctuations in ρ in three different regimes in S1: (a) the $T = 360$ K data represents fluctuations deep into the austenite phase, (b) at $T = 260$ K, where the $\rho - T$ data suggests onset of martensite formation, and (c) at $T = 110$ K, where a substantial drop in the noise magnitude is seen deep into the martensite phase. The corresponding power spectral densities S_ρ of noise are shown in Fig. 2b. Apart from the decrease in magnitude from austenite to martensite we find $S_\rho \sim 1/f^\alpha$, where the frequency exponent $\alpha \sim 1 - 1.2$, and resembles the conventional $1/f$-noise observed in a wide range of disordered metallic thin films[10,11]. We point out that the behavior of S_ρ in stress-driven resistance fluctuations indicated α as large as ~ 3 which was attributed to burst-like dynamics[7].

The T variation of equilibrium noise magnitude is shown for both samples in Fig. 3a. For comparison, the measured S_ρ is normalized to the conventional Hooge parameter γ_H defined as,

$$S_\rho(f) = \frac{\gamma_H \rho^2}{n \Omega f^\alpha}$$

where n, Ω and ρ are number density of atoms, sample volume, and the resistivity of the sample, respectively. Note that the observed magnitude of γ_H is ~ 9 orders of magnitude higher than for typical diffusive metallic
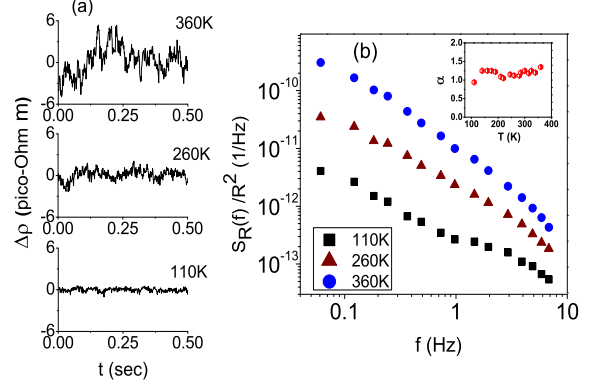
films[12,13]. Fig. 3a shows both heating and cooling cycles. Note that γ_H in S2 is nearly two orders of magnitude larger than that of S1, indicating the pivotal role of defects in producing the fluctuations[14,15].

If noise originates from defect dynamics, the T-dependence of γ_H is expected to be directly proportional to the density of mobile defects[14]. Here, γ_H shows a nearly activated behavior with T deep inside the martensite and austenite regimes (Fig. 3a and 3b), with activation energies of ≈ 0.17 eV and 0.28eV in the martensite and austenite phases respectively. The typical energy scales of defect (void or interstitials) creation in NiTi is 1-2eV[16], however, presence of grains and grain boundaries can modify this energy scale substantially. Moreover, contributions from additional mechanisms, such as interference effects[17], cause noise to deviate from pure activated form at very low T ($\ll M_f$).

A striking feature in the behavior of γ_H is the weak or slightly decreasing T-dependence over $\sim 200 - 300$ K, irrespective of heating or cooling cycle. From the $\rho - T$ data (Fig. 1) we find this region to appear between M_s and M_f for both samples. A plausible mechanism leading to the slow variation of γ_H between M_s and M_f may involve a two-phase coexistence during martensite formation. Assuming individual Hooge parameters to be γ_H^A and γ_H^M in the austenite and martensite regions respectively, the net Hooge parameter at an intermediate T, $M_s > T > M_f$, can then be phenomenologically expressed as $\gamma_H = f \gamma_H^M + (1-f) \gamma_H^A$, where f is the fraction of martensite region that changes from $0 \rightarrow 1$ as T varies from $M_s \rightarrow M_f$, resulting in a weakly varying γ_H as observed in the transition regime. XRD data also confirms the coexistence of the martensite and austenite at room temperature in sample S2, although the signature of austenite was weak in S1. Alternatively, a partial annealing of defects[14], may also occur as the crystal reori-
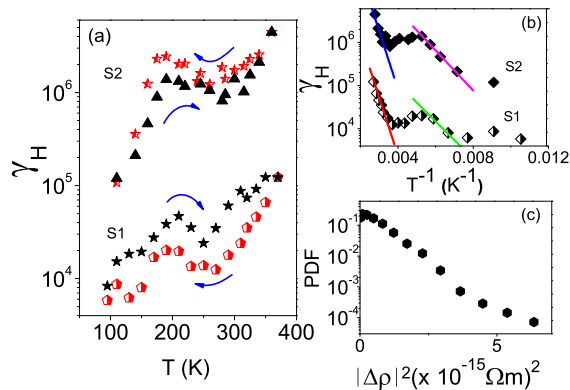
FIG. 3: (a) Hooge Parameter γ_H vs T for both the samples. Note that the regions at the two ends are linear and the middle portion is flattened out. (b) The activated behaviour of the two phases for samples $S1$ and $S2$ during cooling. (c) Normalised Probability Density Function (PDF) vs. $\Delta\rho^2$ for S1.

ents between M_s and M_f resulting in a weakly decreasing γ_H with increasing T in the heating cycle. Similar behavior in the cooling cycle possibly indicates generation of new defects, as the crystals transform from high symmetry austenite to low symmetry martensite phase. Nevertheless, the sharp changes in the T-dependence of noise at the beginning and end of the martensite allows independent estimates of M_s and M_f.

Another crucial aspect of the data shown in Fig. 3a is the pronounced hysteresis in the noise data between heating and cooling cycles, where the range of hysteresis in T largely exceeds that observed in the simple $\rho - T$ measurements (Fig. 1). This is particularly surprising considering the equilibrium nature of the noise measurement. We believe its origin lies in substantial modification of the transformation temperature scales along the grain boundaries in NiTi thin films. The interaction of the martensitic plates with grain boundaries would not only be sensitive to the grain size, but also the physical structure of the grains, leading to a wide distribution of M_s, M_f, A_s and A_f along the grain boundaries[3,18]. The sensitivity of noise to local microstructures and corresponding energy scales can be readily understood, if we assume noise to be primarily due to diffusion of defects along the grain boundaries. Time-averaged resistivity ρ, on the other hand, is determined by electron scattering in the bulk of the grains as well, and less sensitive to the nature of microstructure at the grain boundaries.

The intriguingly large magnitude of γ_H in both samples is unlikely to arise from coupling of electron transport to uncorrelated defect dynamics. Long range correlations, such as many-body Coulomb interactions in doped semiconductors[19], however has been known to result in large γ_H. In NiTi thin films such correlations may appear in the form of a long range elastic potential[20], in which defect dynamics takes place. This may also con-

tribute a non-Gaussian component in the kinetics of resistance fluctuations. We have plotted the probability distribution function of the fluctuations in the transition region (170 K − 290 K), in Fig. 3c. In spite of relatively large device dimensions (1×10^{17} atoms), existence of a weak non-Gaussian tail indeed suggests a correlated dynamics of defects. Note that the premartensitic fluctuations[5] or the displacive motion of twin boundaries in NiTi are primarily athermal, and hence not expected to have a significant effect at long time scales.

In conclusion, we have investigated the equilibrium low-frequency resistivity fluctuations, or noise, in the thin films of NiTi shape memory alloys. The noise magnitude was found to be unusually large, and displays signature of the martensite transformation on the dynamics of structural defects. Our investigations suggest independent estimates of the martensite transformation temperature scales from a direct microscopic mechanism that agree with those obtained from resistivity and other structural characterizations.

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